Volatile Losses from Aged Field Sediments

PURPOSE: This technical note describes laboratory investigations conducted to obtain flux data from contaminated aged field sediments and a laboratory spiked sediment for the emission of volatile organic chemicals (VOCs) from sediment exposed to the atmosphere. These data are being used to develop and validate predictive volatile emissions models. Laboratory experimental techniques and results obtained are presented.

BACKGROUND: The loss of volatile contaminants from sediments and dredged materials is an increasingly recognized environmental problem. Disposal and storage operations associated with dredged material placement in confined disposal facilities (CDFs) can increase the opportunity for VOC emissions. Previous investigations conducted at the U.S. Army Engineer Waterways Experiment Station (WES) with New Bedford Harbor sediment revealed high VOC emissions when the material was disturbed and exposed to air (Thibodeaux 1989). Until recently, flux data obtained from field sediments have not been available to verify models developed to accurately predict VOC emissions from sediments under different environmental and operational conditions. Mathematical modeling tools to estimate potential volatile emissions from contaminated dredged sediments are needed in order to develop guidelines to control possible contaminant volatile emissions during dredging and disposal.

INTRODUCTION: Dredging, disposal, and placement operations in CDFs can increase the potential for volatile emissions from contaminated sediments. Valsaraj et al. (1995) surveyed the various locales and pathways for sediment-to-air mass transfer of contaminants and concluded that the most significant locale for air emissions is the exposed sediment. The emission of volatile and semi-volatile organic compounds from exposed contaminated dredged materials is known to depend upon a variety of factors (Valsaraj et al. 1997). Sediment physical characteristics, such as aging, porosity, moisture content, and percent oil and grease can play a significant role in controlling volatile emissions from sediments. Contaminant chemical properties such as Henry s Law Constant and vapor pressure are also very important in determining contaminant flux to air. Environmental variables such as relative air humidity and temperature can also play major roles in contributing to volatile losses.

Several mathematical models have been developed for estimating air emission rates from exposed sediments under a variety of sediment physical conditions (Valsaraj et al. 1997, Ravikrishna et al. 1998, Choy and Reible 1998). These models are evaluated with data generated at the WES Environmental Laboratory and Louisiana State University (LSU) Department of Chemical Engineering, in laboratory investigations using both laboratory-spiked and field sediments.

MATERIALS AND METHODS

• **Sediment.** Three contaminated field sediments and one uncontaminated laboratory-spiked sediment were used in the experiments described here. The uncontaminated sediment (UL) was obtained from University Lake, Baton Rouge, LA, and was spiked with the contaminants of concern. The three contaminated sediments from field sites were chosen because of their interest to the U.S. Army Corps of Engineers. These sediments were obtained from areas that are planned for dredging and disposal in CDFs and include: (a) sediment obtained from the Indiana Harbor Canal (IHC), (b) sediment obtained from the Grand Calumet River (GCR), and (c) sediment obtained from New York Harbor (NYH). The properties of all four sediments are given in Table 1. Of particular interest is that two of the field sediments, IHC and GCR, contain significant percentages of oil and grease.

Table 1 Physical and chemical properties of sediments				
Property	IHC	GCR	NYH	UL
Moisture Content	54	62	53	26
Percent sand	45	75	57	3
Percent silt	46	17.5	37	41
Percent clay	8	7.5	5	56
Percent total organic carbon	2.6	5.4	2.7	3.0
Percent oil and grease	1.0	1.4	0.03	0
Porosity, cm^3/cm^3	0.78	0.83	0.7	0.52
Bulk density, g/cm^3	0.6	0.51	0.66	1.2
Naphthalene, mg/kg	38	586	0.2	NA
Phenanthrene, mg/kg	51	432	0.9	97
Pyrene, mg/kg	59	172	1.9	94
Dibenzofuran, mg/kg	NA	NA	NA	108
TRPH, mg/kg	12790	54000	287	0

Volatile emissions experiments with Indiana Harbor Canal sediment and Grand Calumet River sediment were conducted for the Chicago District and included testing for polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), ammonia, hydrogen sulfide, and methyl mercaptans. New York Harbor sediment experiments were conducted for the New York District and volatile emissions were measured for PAHs, PCBs, pesticides, and dioxins.

For model validation and experimental purposes when conducting tests with UL sediment, four compounds were chosen as representative VOCs due to their prevalence in contaminated sediments. The selected representative contaminants in these investigations included three PAHs (naphthalene, pyrene, and phenanthrene (PHE)) and one heterocyclic aromatic compound, dibenzofuran (DBF).

• **Flux Chambers.** All tests were conducted using VOC flux chambers designed by LSU and constructed at WES and LSU (Figure 1). The two-piece aluminum anodized chambers were devised to hold a 10-cm depth of sediment with a surface area of 375 cm^2. The chambers were sealed with an O-ring and threaded fasteners for an airtight fit.
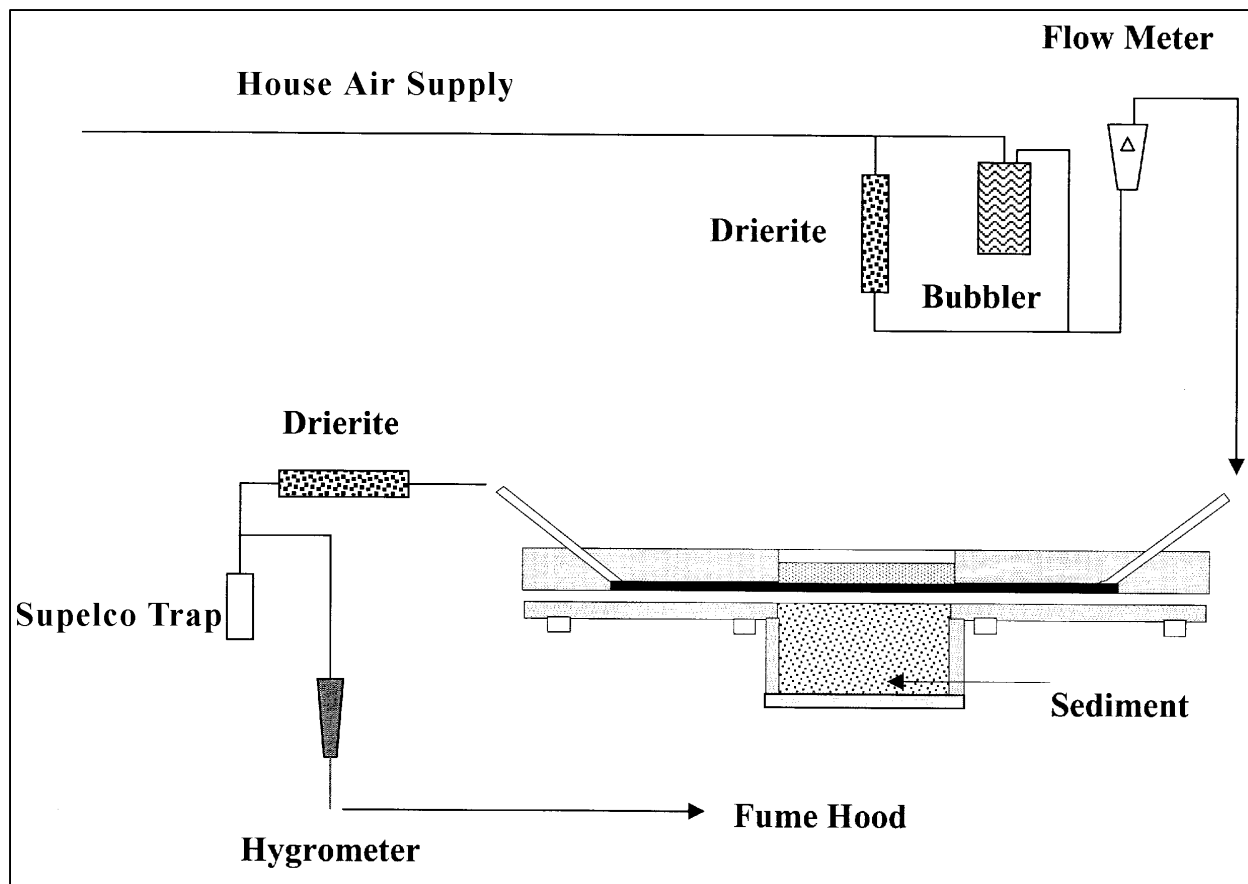
Figure 1. Experimental flux chamber schematic

Contaminant-specific adsorbent-filled air sampling traps (Orbo 44, Supelco Inc., PA) were attached to the chamber exit ports. Traps were removed from the exit lines at the end of each sampling interval, and solvent was extracted and analyzed according to U.S. Environmental Protection Agency (EPA) method 8270 (USEPA 1982). Development of the laboratory procedures used for all experiments herein is described in Price et al. (1997).

Contaminant flux [$N_A(t)$] through the chambers was calculated by determining the total mass of material captured in a given time interval using the equation

$$N_A(t) = \frac{\Delta m}{\Delta t A_c}$$

where

Δm = mass (ng) of compound collected on the trap in time Δt (hr)

A_c = area of the sediment-air interface, cm^2

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$N_A(t)$ is expressed in ng/cm^2/hr

- **Experimental Design.** Flux chambers were filled with a known weight (wet weight) (approximately 2,100 grams) of sediment and sealed. Air was passed over the sediment surface at 1.7 L/min and relative humidity was maintained by using an in-line bubble trap to add moisture vapor as determined by experimental protocol. A thermohygrometer (Cole-Parmer) was connected to the exit port to monitor exit air temperature and relative humidity.

Experiments with UL sediment conducted at LSU were designed to formulate comparisons of contaminant fluxes between a laboratory-spiked sediment and naturally contaminated sediments. Experimental procedures were designed to determine the effects of changes in sediment moisture content and relative air humidity on volatile emissions (Valsaraj et al. 1999).

Experiments were conducted with the field sediments to provide information on maximum contaminant fluxes expected under different air humidity and sediment moisture conditions that might occur during CDF operations. In addition, the IHC and GCR sediment experiments included additional testing to determine the effects of sediment disturbance on volatile emissions.

The sampling schedule for IHC and GCR sediments consisted of five continuous runs simulating various environmental and operational scenarios. All runs were performed on a single sediment sample in series. Runs I and II gave maximum initial contaminant fluxes from wet sediment (at field moisture) under dry and humid air conditions. Dry air was passed over the sediment surface for 14 days for Run I, after which the relative humidity of the air was increased to 98 percent and samples were taken for another 7 days for Run II. Run III simulated a rainfall event in which the sediment was rewet to near field capacity and dry air was passed over the sediment for an additional 14 days. Run IV represented the occurrence of mechanical mixing during CDF operations. The sediment was reworked in a glove chamber equipped with sampling tubes to trap contaminants released during mixing. Dry air was then passed over the sediment for another 7 days. The sediment was rewet again to near field capacity for Run V, and dry air was again passed over the sediment surface for a final 7 days. Air samples were taken at 6, 24, 72, and 168 hr in all five runs, and at 240 and 336 hr for the 14-day sampling periods (Runs I and III).

The sampling schedule for NYH sediment consisted of four continuous runs. The experimental scenario was identical to that for IHC and GCR sediments in Runs I and II. After Run II, the sediment was rewet to near field capacity and humid air was passed over the sediment for 14 days. The humid air was changed to dry for Run IV and samples were taken for an additional 7 days. Air samples were taken as previously described for IHC and GCR experiments.

RESULTS AND DISCUSSION

- **Experimental Fluxes from Aged Field Sediments.**

  - **PAH Fluxes.** The majority of hydrocarbon fluxes from the three sediments described in these experiments exhibited sharp initial decreases in flux in the first 24 to 48 hr after passage of dry air over the sediment surface (Run I). Figure 2 shows PHE flux from each sediment tested. These flux rates and trends are characteristic for the majority of PAH compounds detected in the exit air of these

experiments. The trends in flux are indicative of a diffusive transport from the sediment to air. As the sediment surface dries, there is little competition for sorption sites and flux thereby decreases to low levels.
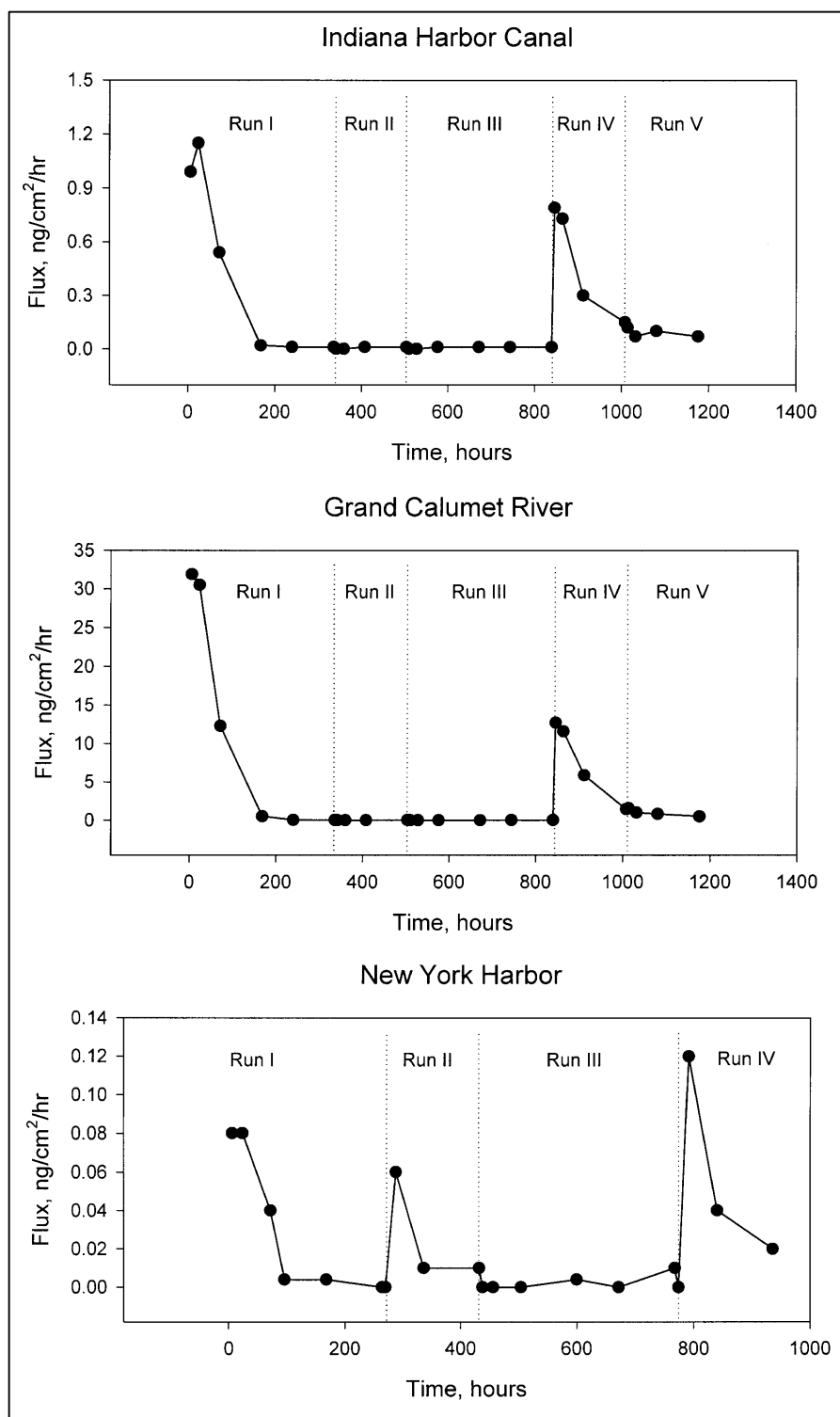

Figure 2.   Phenanthrene flux rates from IHC, GCR, and NYH sediments

In Run II the relative air humidity was increased to approximately 98 percent. No increase in flux was seen in the experiments conducted with the IHC and GCR sediments. Apparently the oil and grease in the IHC and GCR sediments formed a thin oil film on the sediment surface, resulting in initial evaporation of the oil and contaminants with the oil, but subsequent diffusion through the oil layer would be much slower than that through pore air spaces (Ravikrishna et al. 1998). Contaminant fluxes increased in the experiment conducted with NYH sediment when humid air was applied (Figure 2). Similar results were noted for UL laboratory-spiked sediment (Ravikrishna et al. 1998). The initial passage of dry air over the sediment surface resulted in increasing the capacity of the sediment surface for contaminant sorption. When the sediment surface is dry, there is little competition for sorption sites for organic contaminants since the moisture content in the air is zero. The contaminant would diffuse slowly through the deeper sediment layers to the surface and the subsequent addition of humid air over the surface would result in water molecules displacing the sorbed organic materials, increasing the contaminant flux to air.

Run III for the IHC and GCR sediments represents a rain event simulated by rewetting the sediment to near field capacity and passing dry air over the sediment surface. No increase in fluxes was noted. Run III for NYH sediment also involved rewetting the sediment but passing humid air over the surface, which resulted in an increase in many PAH emissions. Rewetting the sediment decreases sediment sorptive capacity for contaminants, resulting in an increase in flux. The sediment surface is quickly depleted of contaminants and sediment-side diffusion will take over, causing the flux to drop to a steady state value after a short period of time.

Run IV in the experiments conducted with the IHC and GCR sediments represented reworking of the sediment followed by passage of dry air over the surface and resulted in significant flux increases for the majority of the PAH compounds. The thin oil-film layer on the sediment surface was reestablished after reworking of the sediment, resulting in a new source of contaminant (Ravikrishna et al. 1998; Valsaraj et al., in review). Quick evaporation of this layer would account for the observed flux, but once the initial flux decreased, subsequent emissions would involve diffusion through this oil layer at a slower rate. Run IV for the NYH sediment consisted of decreasing the relative air humidity again, and resulted in increased fluxes for many of the PAH compounds. The mechanism of contaminant transport to air is effectively identical to that in Run I.

Run V for the IHC and GCR sediments consisted of rewetting the sediment and passing dry air over the surface. Again, as in Run III, no increase in PAH emissions was observed.

- **Moisture and Grease Effects**

   - **Laboratory-spiked University Lake sediment.** Experiments conducted at LSU with University Lake sediment were carried out using the sediment at two different moisture contents (6.5 and 26 percent) (Valsaraj et al. 1997; Ravikrishna et al. 1998; Valsaraj, in review). Sediment with a moisture content greater than 6.5 percent is considered to be "wet," meaning that the pore air space is saturated (de Seze et al. 1998). Results showed that the long-term flux of PAHs from the 26-percent moisture sediment was lower than from the 6.5 percent (Figures 3a, 3b, and 3c). Similar results were also revealed in separate experiments conducted with NYH sediment (Valsaraj 1998). Also presented in these figures are two separate model fits using two different surface mass transfer

coefficients (k_a). The chemodynamic model and analytical equations used for the sediment microcosm experiments described in this note are detailed in Valsaraj et al. (1999). As can be seen in Figures 3a to 3c, the model predictions for PAH fluxes are in excellent agreement with the experimental data obtained. Also presented in Figure 3d is the sediment concentration profile (z = depth below sediment surface) in the experiment conducted with 6.5-percent sediment moisture. Both DBF and PHE concentrations (W_A) in the first 10 mm of sediment were significantly lower than those in the deeper layers which had concentrations identical to initial loading concentrations. The final sediment concentration profiles predicted using equations described in Valsaraj et al. (1999) are also given in Figure 3d and it can be noted that the predicted concentrations are in excellent agreement with observed values.
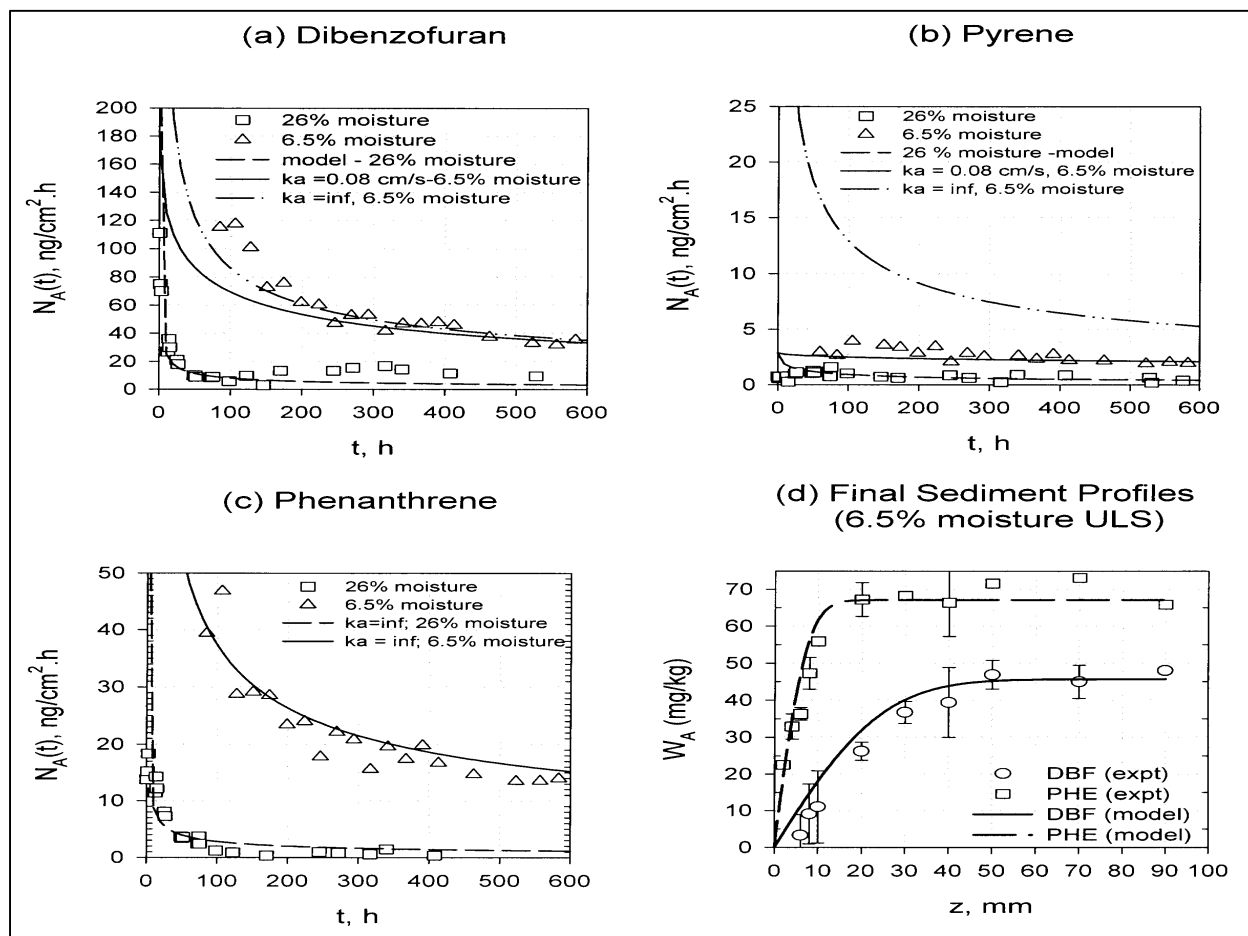

Figure 3. PAH fluxes from University Lake sediment under different moisture conditions

- **Experimental fluxes from laboratory-spiked and field sediments.** In addition to the difference in contaminant aging between the UL and field sediments, two of the field sediments (IHC and GCR) contained significant concentrations of oil and grease (1.0 and 1.4 percent, respectively). The NYH sediment contained a very small concentration of oil and grease (0.03 percent) and the UL sediment contained none. The presence of this oil and grease significantly affected fluxes from the IHC and GCR sediments.

Figures 4a and 4b present experimental flux data and model predictions for all four sediments for naphthalene and pyrene. These figures compare the mass transfer resistance (C_a^o/N_A) of these compounds from the four sediments studied. These comparisons are for fluxes obtained under identical experimental designs and conditions. Figure 4a shows that the predicted values of mass transfer resistance for naphthalene and pyrene in the UL and NYH sediments are very similar to the experimental data. Mass transfer resistance for both compounds in the field sediments containing oil and grease (IHC and GCR) showed increased resistance compared to model values for both compounds after 30 hr of passage of dry air over the sediment surface (Figure 4b). Although other PAH compounds showed similar behavior, only two are presented in order to reduce the complexity of the figure.
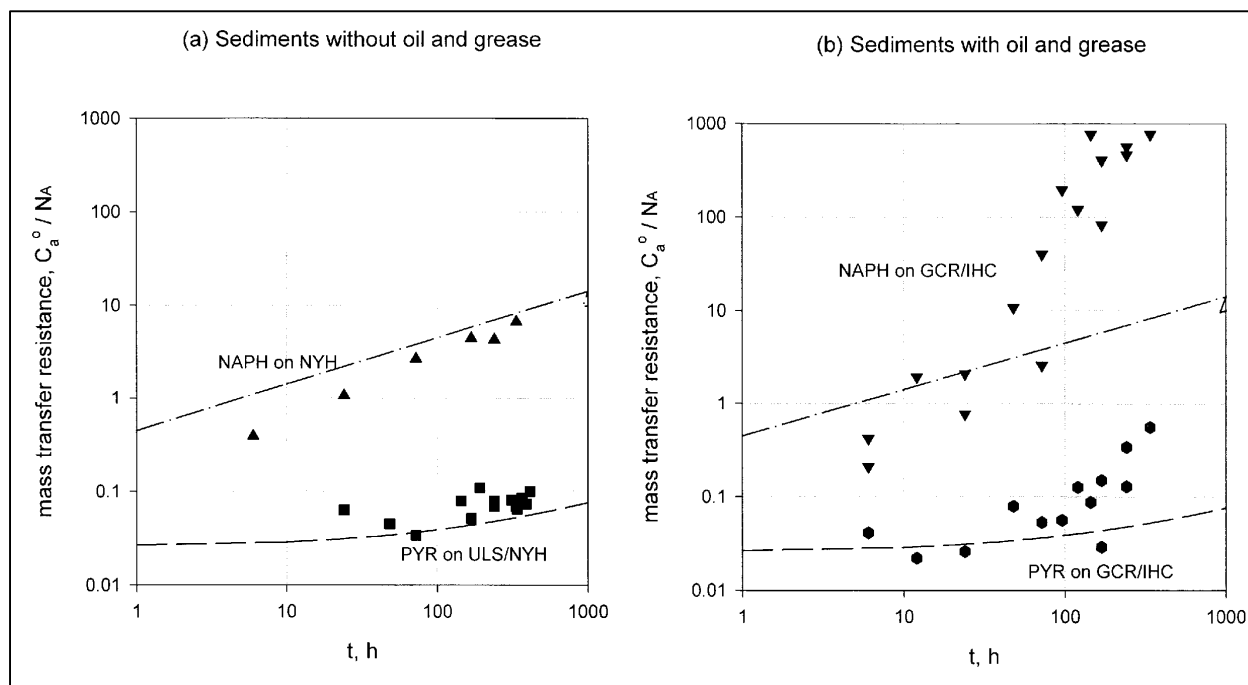

Figure 4. Naphthalene and pyrene experimental flux data and model predictions for field sediments and UL sediment

It was hypothesized that the oil and grease in GCR and IHC sediments contributed to the increased mass transfer resistance of the compounds. The experiments discussed here consisted of dry air being passed over the sediment surface, resulting in the evaporation of the surface water, which would lead to a high concentration of oil and grease in this upper surface layer. The contaminants present in the oil and grease would quickly evaporate upon exposure to air and additional transport of contaminants to the surface via diffusion would be much slower through the oil layer, resulting in decreased fluxes to negligible values.

CONCLUSIONS: Results of these investigations revealed that the highest contaminant fluxes from sediments containing significant concentrations of oil and grease occurred during the initial loading stages and after mechanical disturbance of the sediment. Wetting of the sediment did not greatly increase emission rates for a majority of the compounds measured in sediments high in oil and

grease. Oil and grease in sediments significantly affected contaminant emissions by substantially increasing contaminant mass transfer resistances, which leads to reduced diffusion of contaminants to the sediment surface. This reduced contaminant fluxes to negligible levels. Measured fluxes for sediments contaminated with oil and grease were orders of magnitude lower than model predictions. Sediments low in oil and grease generally conformed to model predictions. The model is being modified to enable improved predictions of contaminant fluxes for sediments high in oil and grease.

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